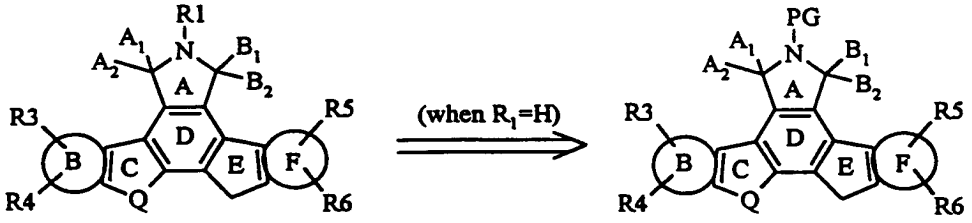
Figure 1.



(3) *(4)*

PG = Protecting Group
or
Polymeric Support

Figure 2.

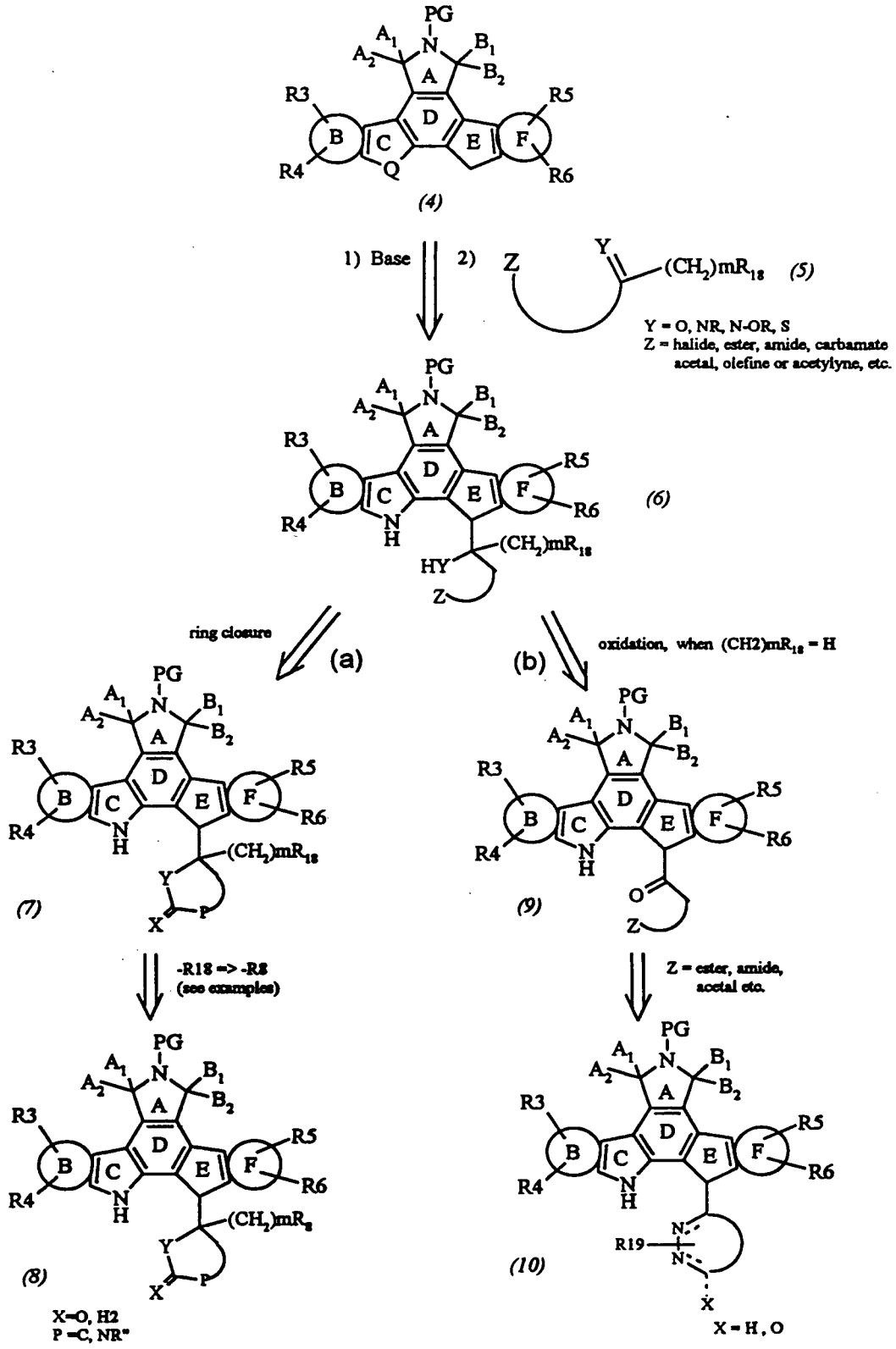

PG
A1
A2
N
B1
B2
A
R3
R5
D
B
C
E
F
R4
Q
R6
(4)
1) Base
2)
Z
Y
(CH2)mR18
(5)
Y = O, NR, N-OR, S
Z = halide, ester, amide, carbamate
acetal, olefine or acetylyne, etc.
(6)
H
HY
Z
ring closure
(a)
(b)
oxidation, when (CH2)mR18 = H
(7)
X
P
(9)
O
-R18 => -R8
(see examples)
Z = ester, amide,
acetal etc.
(8)
X=O, H2
P =C, NR"
(10)
R19
X = H, O

Figure 3. Preparation of Cyclic Substituents via Intra-molecular Dipolar Cycloaddition

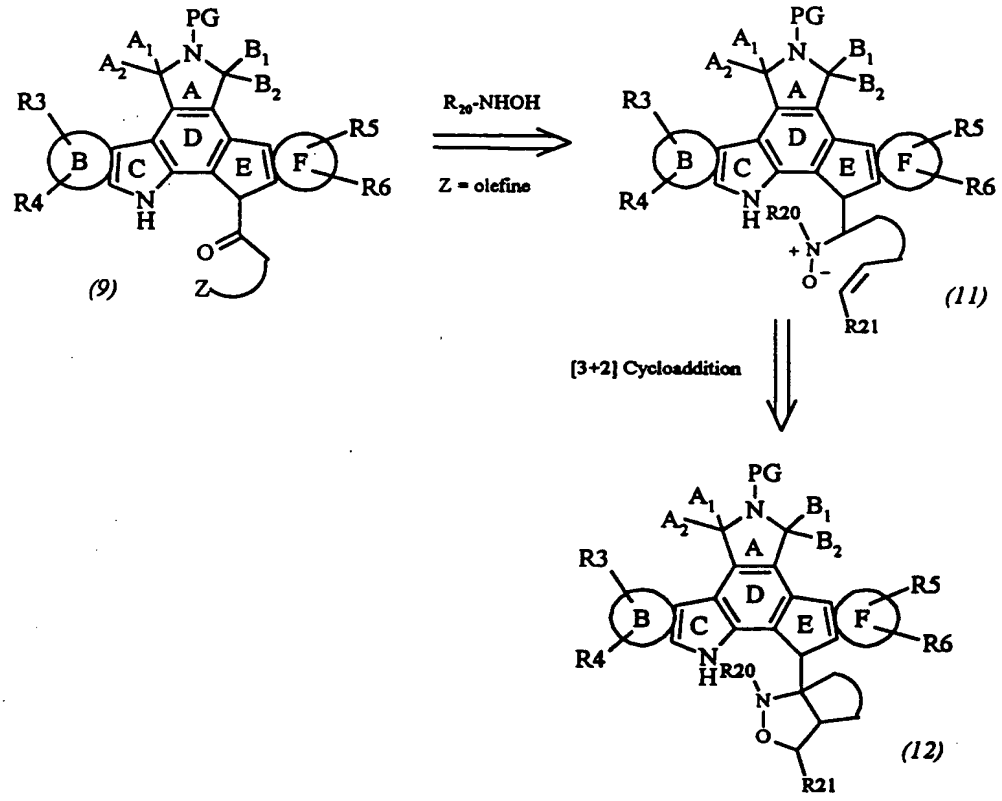


Figure 4. Preparation of Cyclic Substituents via Intra-molecular Dipolar Cycloaddition

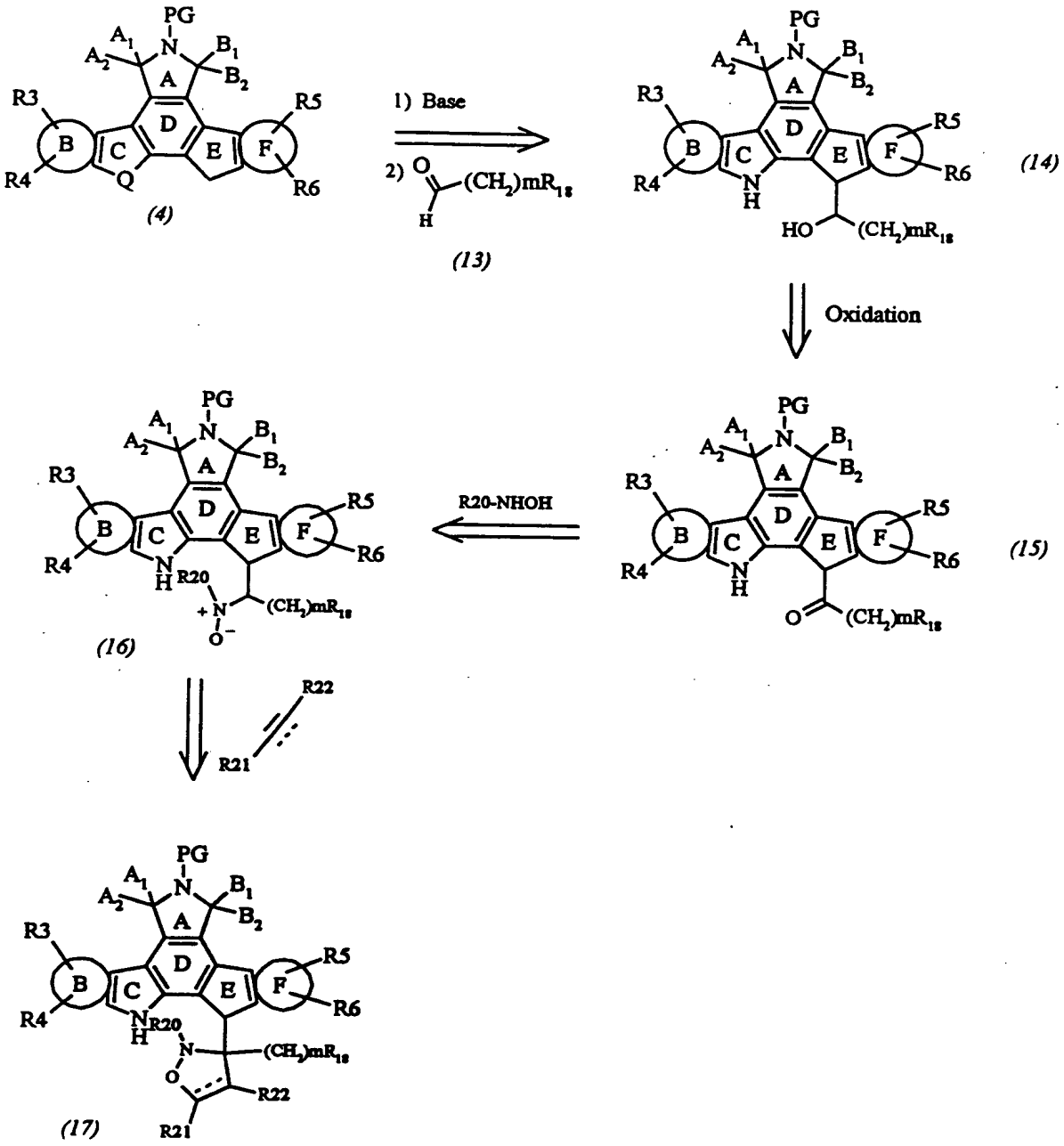


Figure 5.

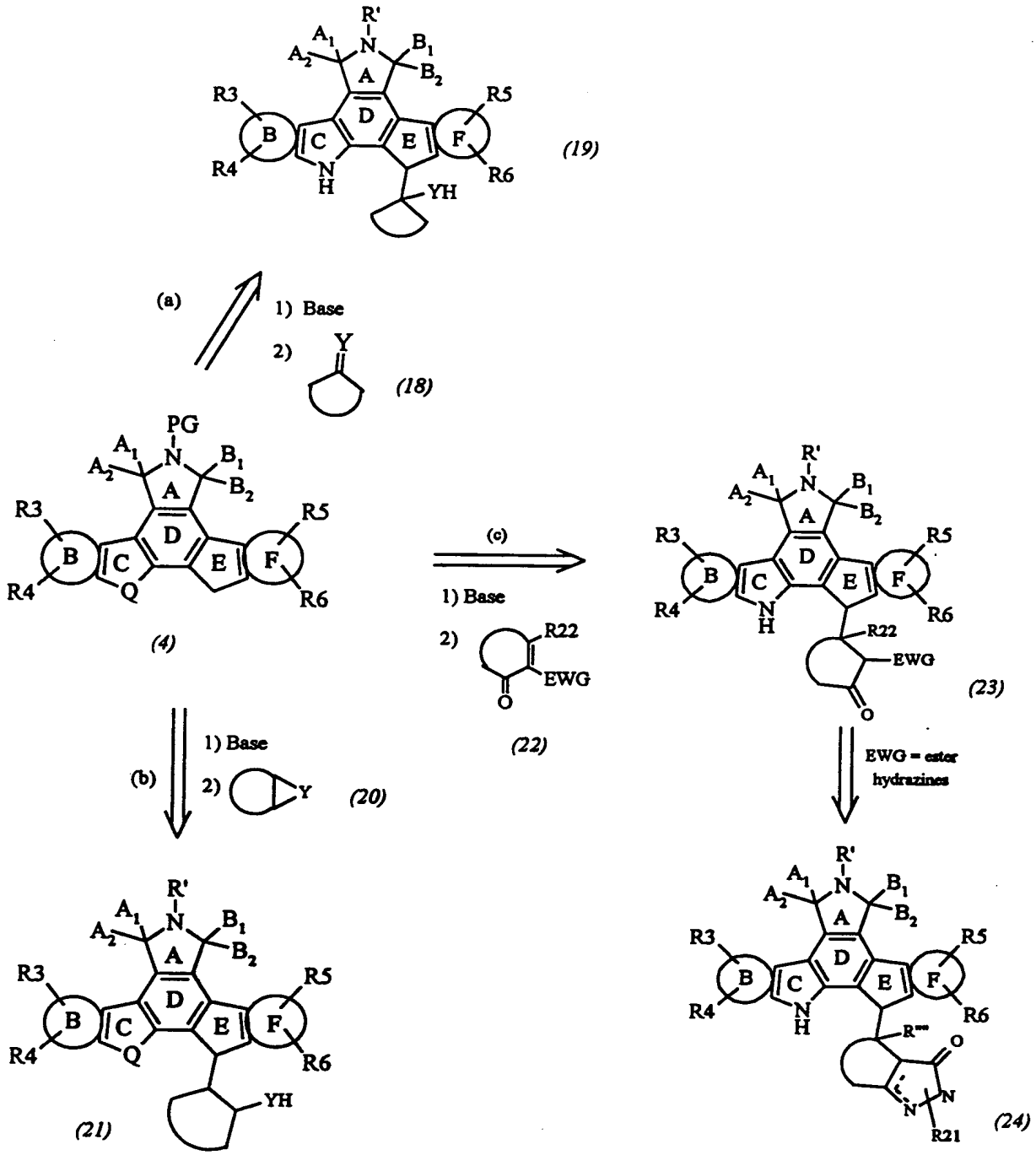

R'
A1
A2
N
B1
B2
A
R3
D
R5
B
C
E
F
R4
N
H
R6
YH
(19)
(a)
1) Base
2)
Y
(18)
PG
(4)
(c)
1) Base
2)
R22
EWG
O
(22)
(23)
EWG = ester
hydrazines
(b)
1) Base
2)
Y
(20)
Q
(21)
R''
O
N
R21
(24)

Figure 6.

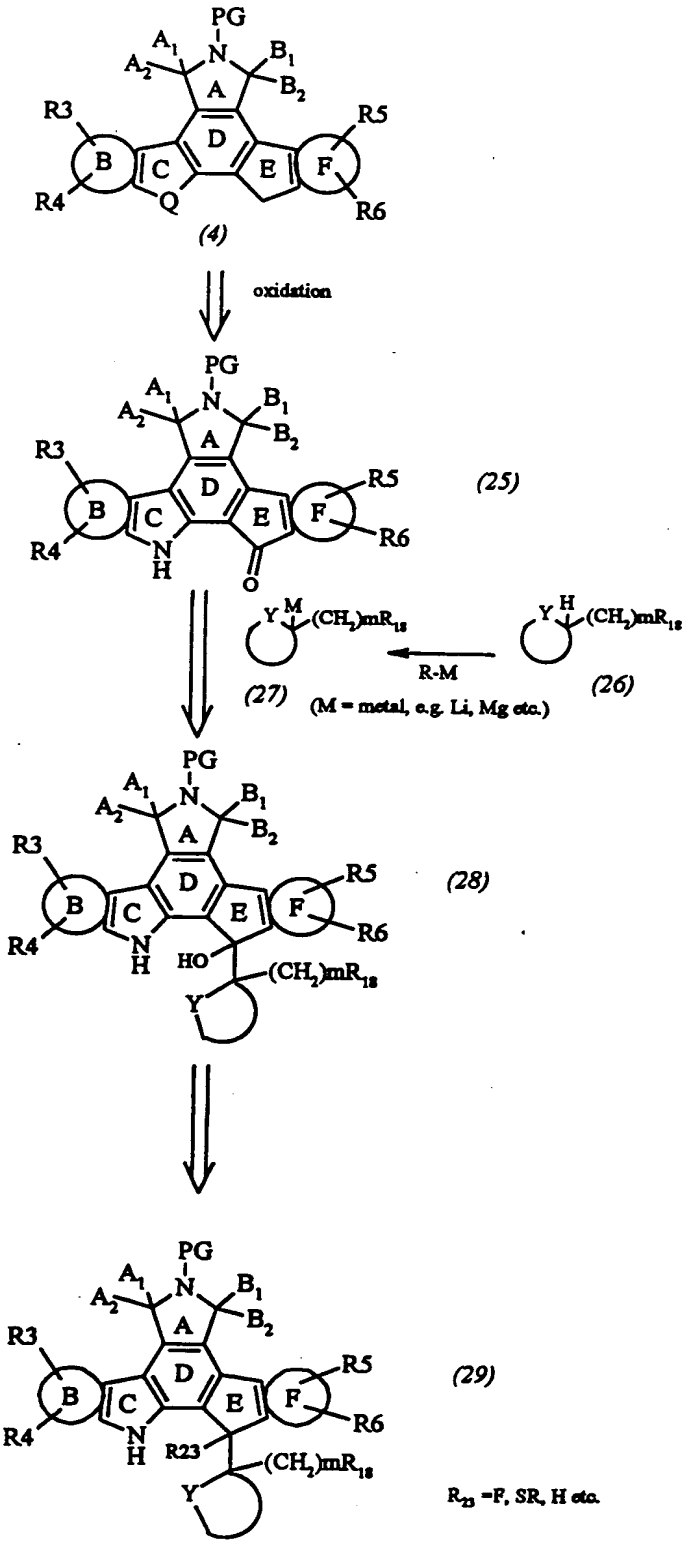

PG
A1
A2
N
B1
B2
A
R3
R5
D
B
C
E
F
R4
Q
R6
(4)
oxidation
(25)
H
O
(CH2)mR18
R-M
(26)
(27)
(M = metal, e.g. Li, Mg etc.)
HO
(28)
R23
(29)
R23 =F, SR, H etc.

Figure 7.

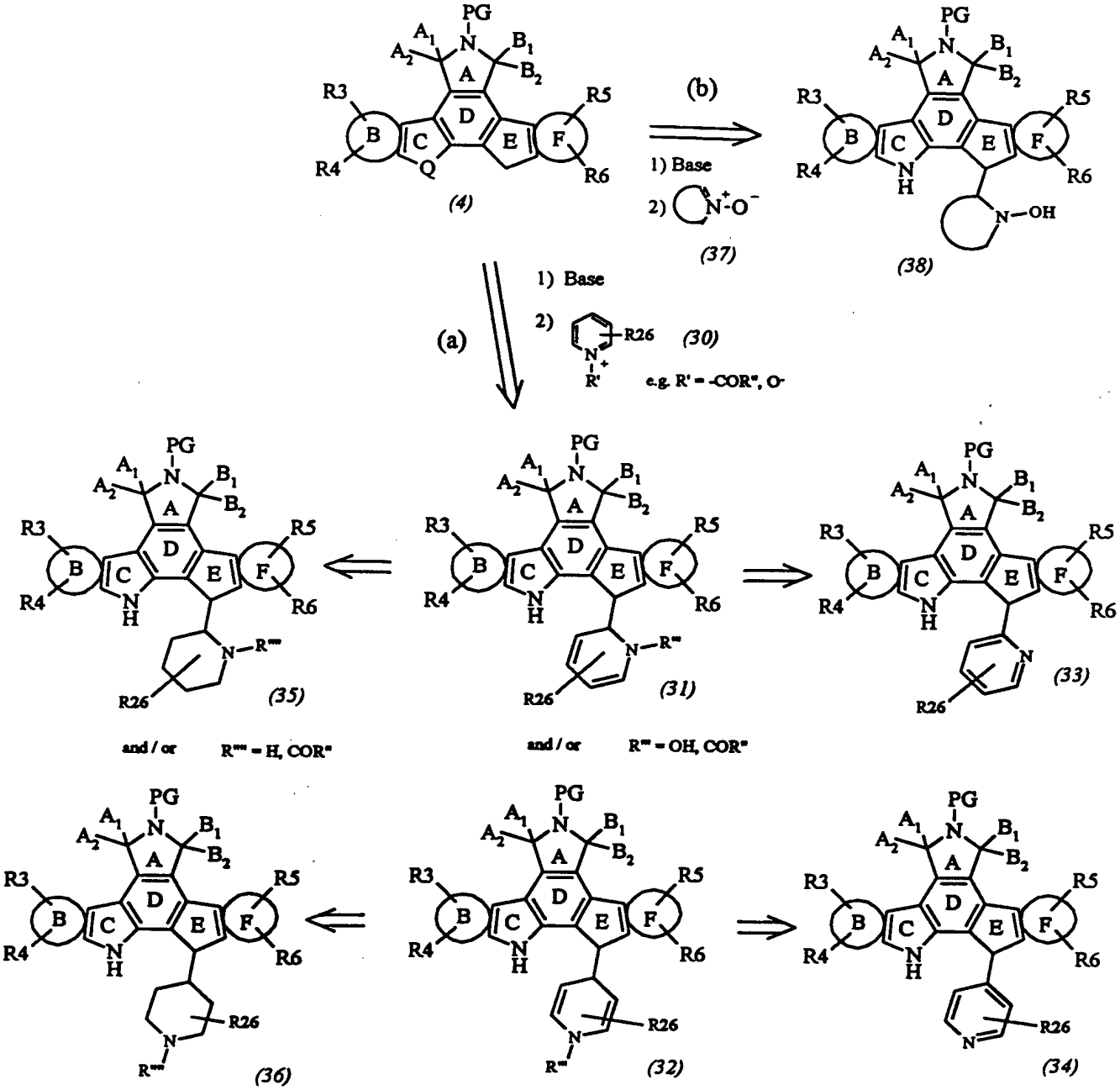
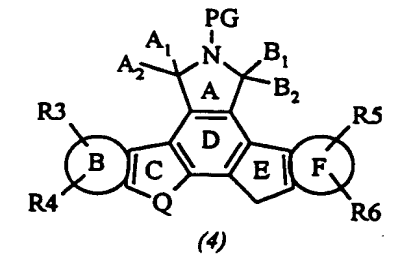
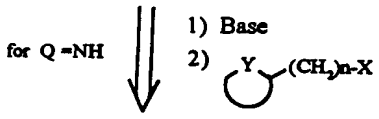

PG
A1
A2
B1
B2
A
D
R3
R4
B
C
Q
E
F
R5
R6
(4)
(b)
1) Base
2)
(37)
(38)
N–OH
(a)
1) Base
2)
R26
(30)
e.g. R' = -COR'', O-
N
H
R'''
(35)
(31)
(33)
and / or
R''' = H, COR''
and / or
R''' = OH, COR''
(36)
(32)
(34)

Figure 8.

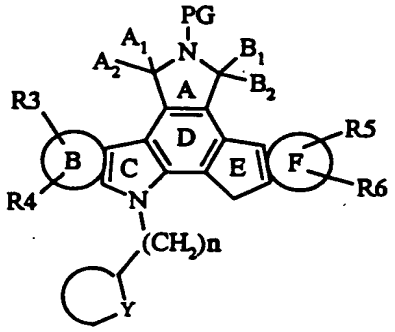


(4)

PG = Protecting Group
or
Polymeric Support



(39)



(40)

Figure 9.

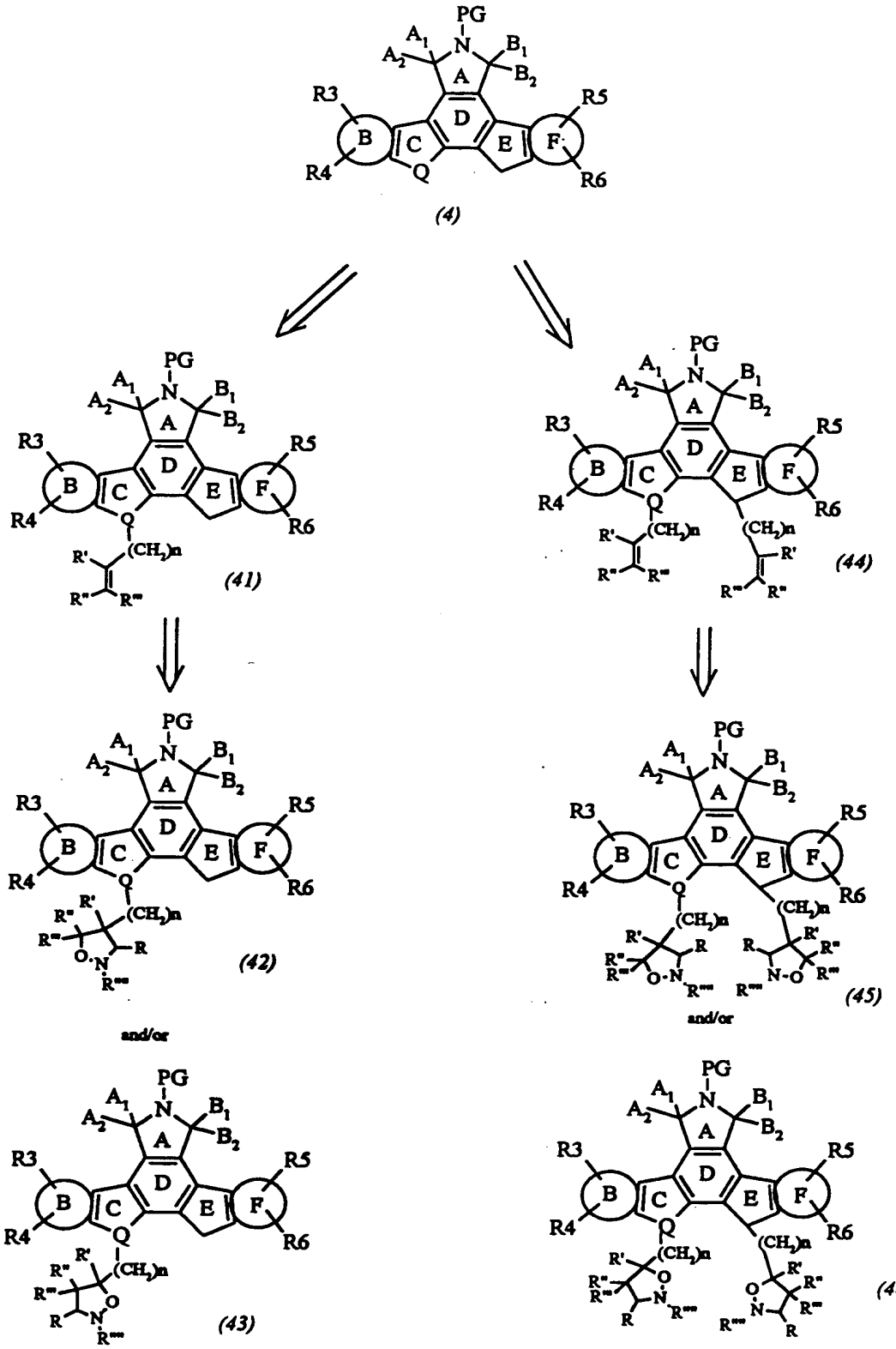
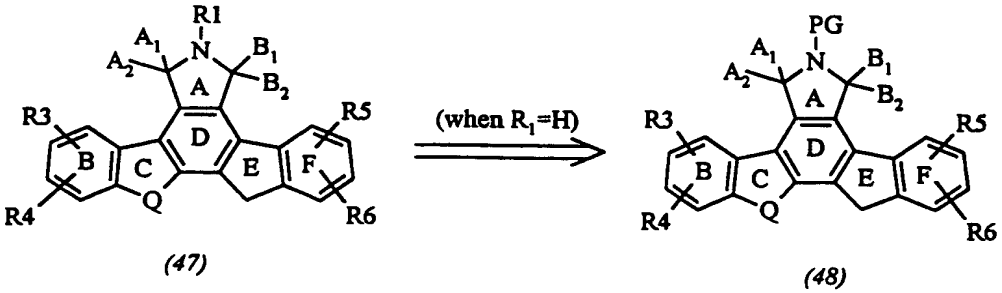
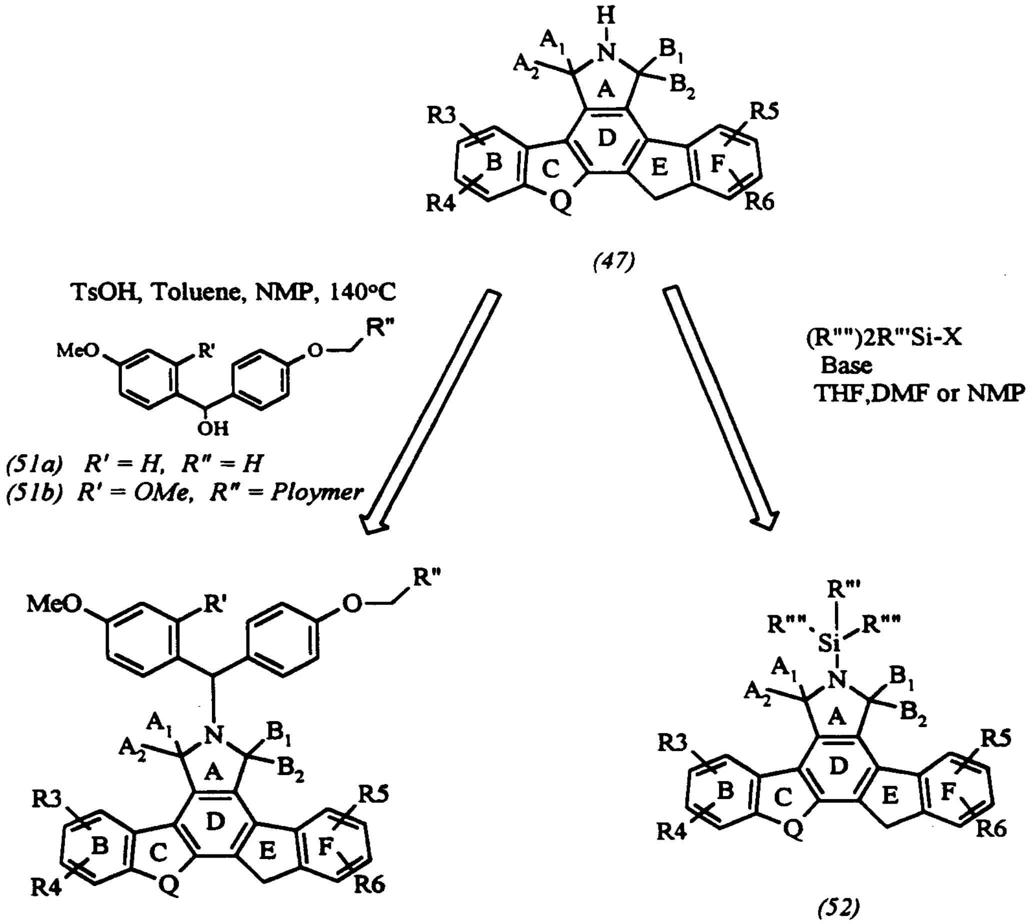


Figure 10.



PG = Protecting Group
or
Polymeric Support

Figure 11. Preparation of Solu[illegible]nd Resin-bound N-lactam protected [illegible]d Pyrrolocarbazoles (FP)



(49) R' = H, R" = H >> soluble protected FP (N-protecting group abbreviated as DMB)

(50) R' = OMe, R" = Polymer >> solid-bound PG (the resin reagent reffered to as Rink-acid resin) This is reffered to ion the text as "Resin"

(e.g. Polymer = copolystyrene-1%divinylbenzene)

R"" = Me, R"' = tBu (TBS)
R"" = Ph, R"' = tBu (TPS)

Figure 12.

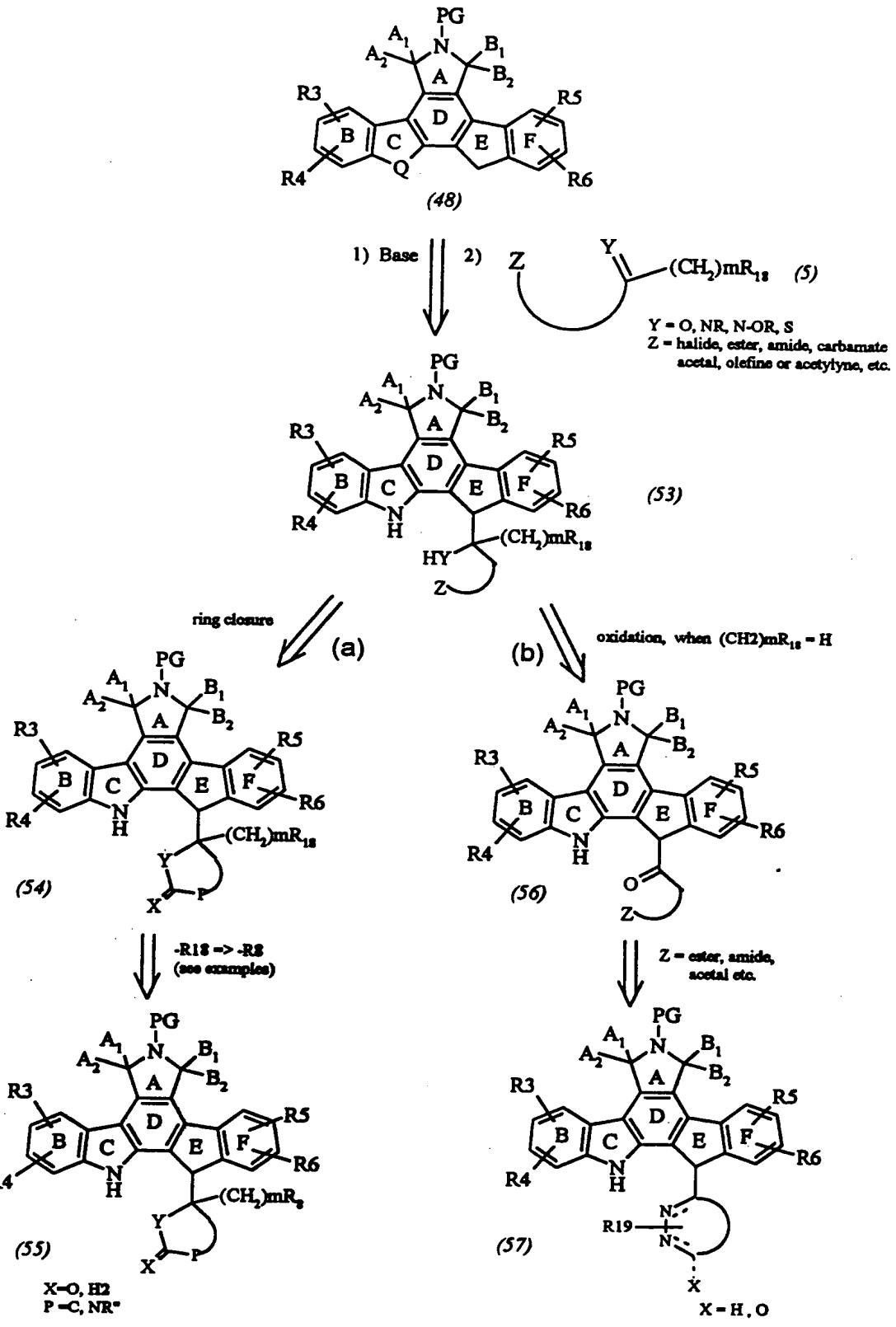

PG
A1
A2
N
B1
B2
A
R3
R5
D
B
C
E
F
Q
R4
R6
(48)
1) Base
2)
Z
Y
(CH2)mR18
(5)
Y = O, NR, N-OR, S
Z = halide, ester, amide, carbamate
acetal, olefine or acetylyne, etc.
(53)
HY
ring closure
(a)
(b)
oxidation, when (CH2)mR18 = H
(54)
(56)
-R18 => -R8
(see examples)
Z = ester, amide,
acetal etc.
(55)
(57)
R19
X=O, H2
P =C, NR"
X = H, O

Figure 13. Preparation of Cyclic Substituents via Intra-molecular Dipolar Cycloaddition

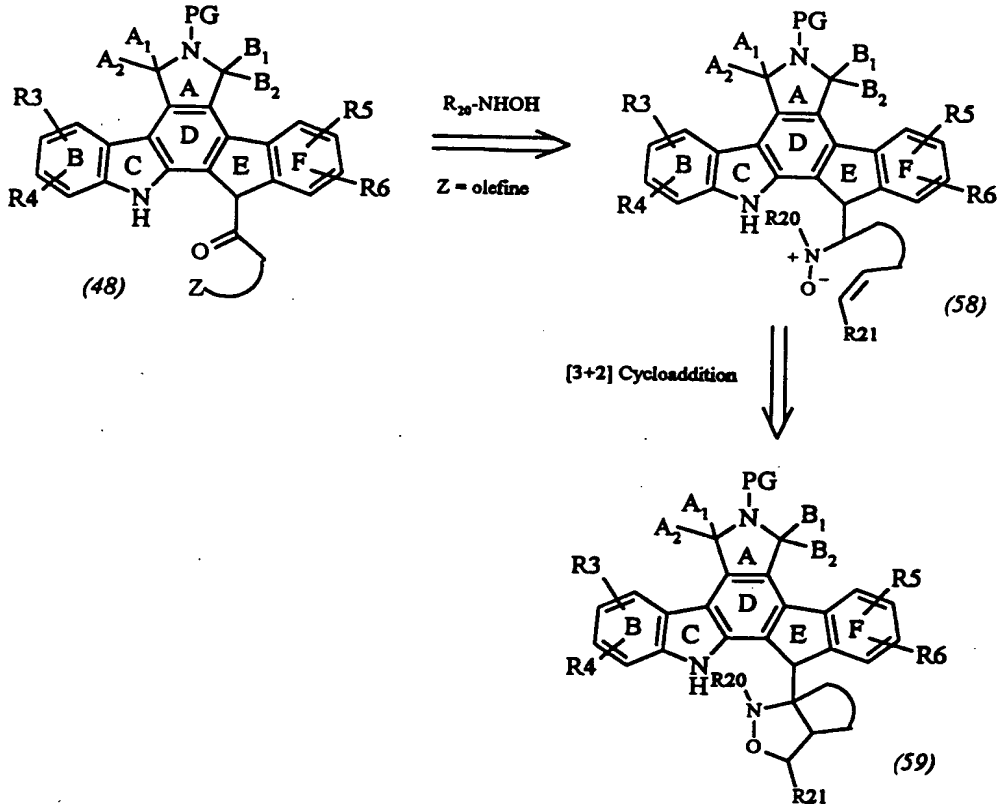


Figure 14. Preparation of Cyclic Substituents via Intra-molecular Dipolar Cycloaddition

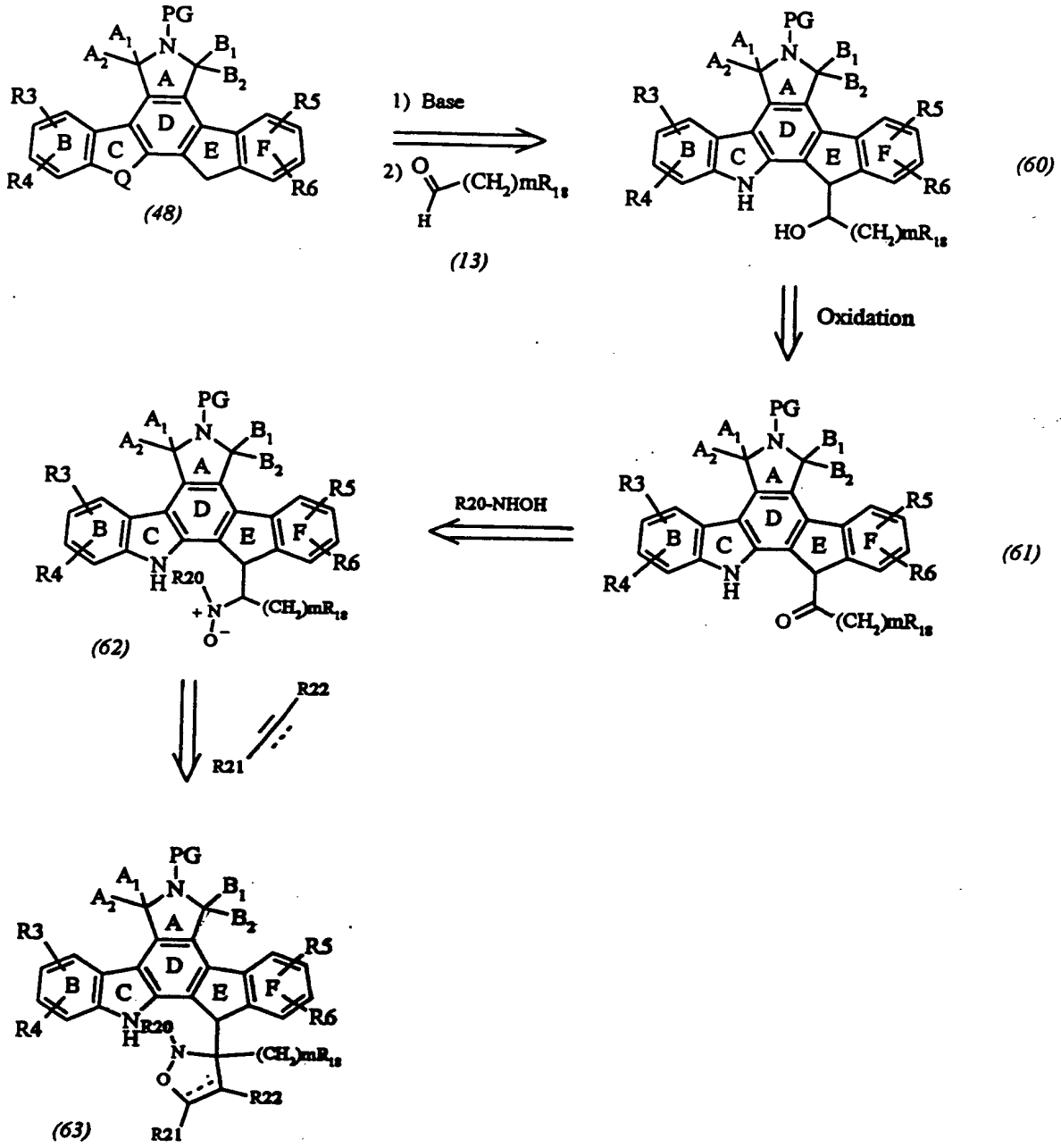


Figure 15.

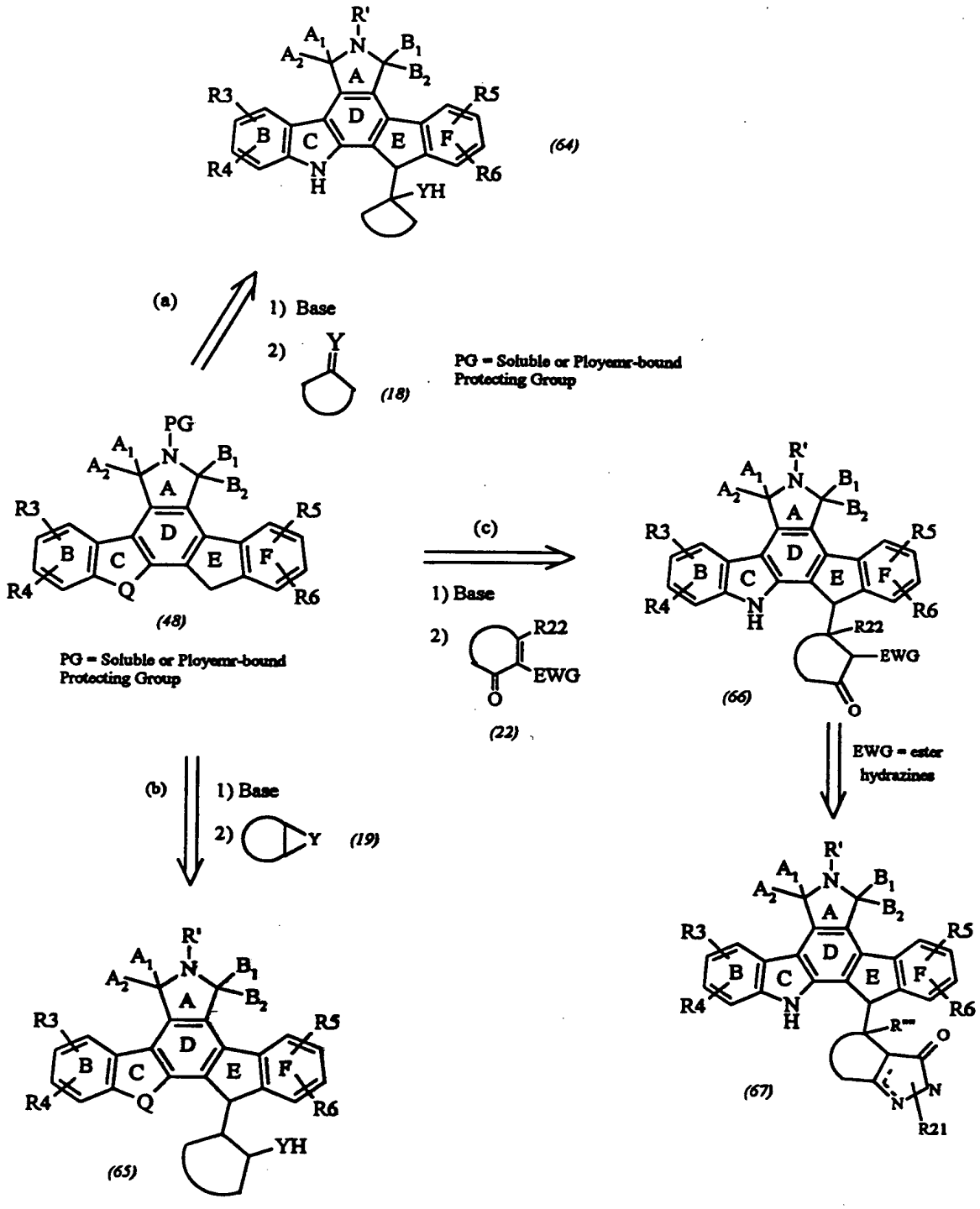

(64)
(a)
1) Base
2)
(18)
PG = Soluble or Ployemr-bound Protecting Group
(48)
PG = Soluble or Ployemr-bound Protecting Group
(c)
1) Base
2)
(22)
(66)
EWG = ester hydrazines
(b)
1) Base
2)
(19)
(65)
(67)

Figure 16.

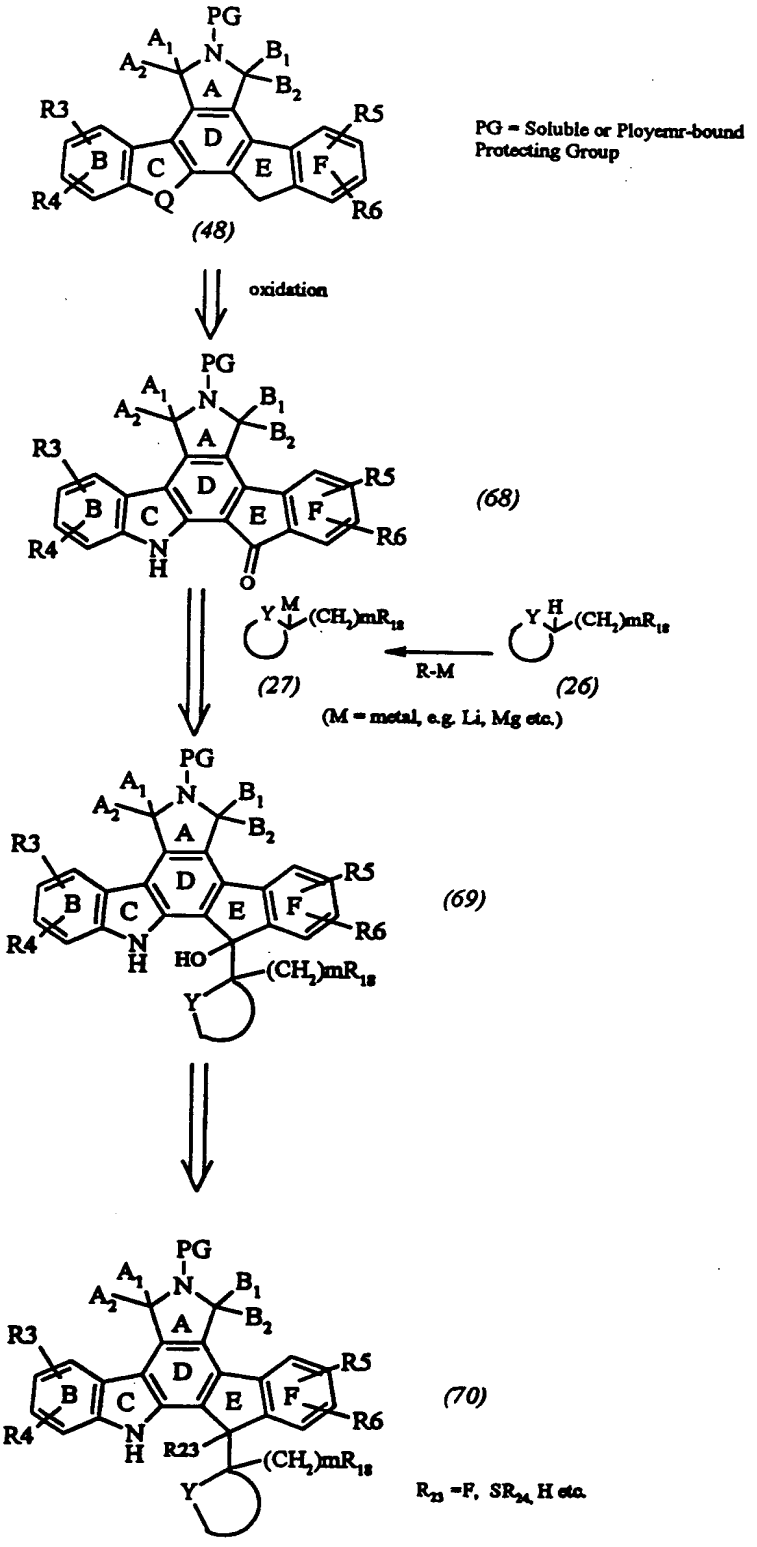

PG
A1
A2
N
B1
B2
A
R3
R5
D
B
C
E
F
R4
Q
R6
(48)
PG = Soluble or Ployemr-bound Protecting Group
oxidation
PG
A1
A2
N
B1
B2
A
R3
R5
D
B
C
E
F
R4
N
H
R6
O
(68)
Y M (CH2)mR18
Y H (CH2)mR18
R-M
(27)
(26)
(M = metal, e.g. Li, Mg etc.)
PG
A1
A2
N
B1
B2
A
R3
R5
D
B
C
E
F
R4
N
H
R6
HO
(CH2)mR18
Y
(69)
PG
A1
A2
N
B1
B2
A
R3
R5
D
B
C
E
F
R4
N
H
R6
R23
(CH2)mR18
Y
(70)
R23 =F, SR24, H etc.

Figure 17.

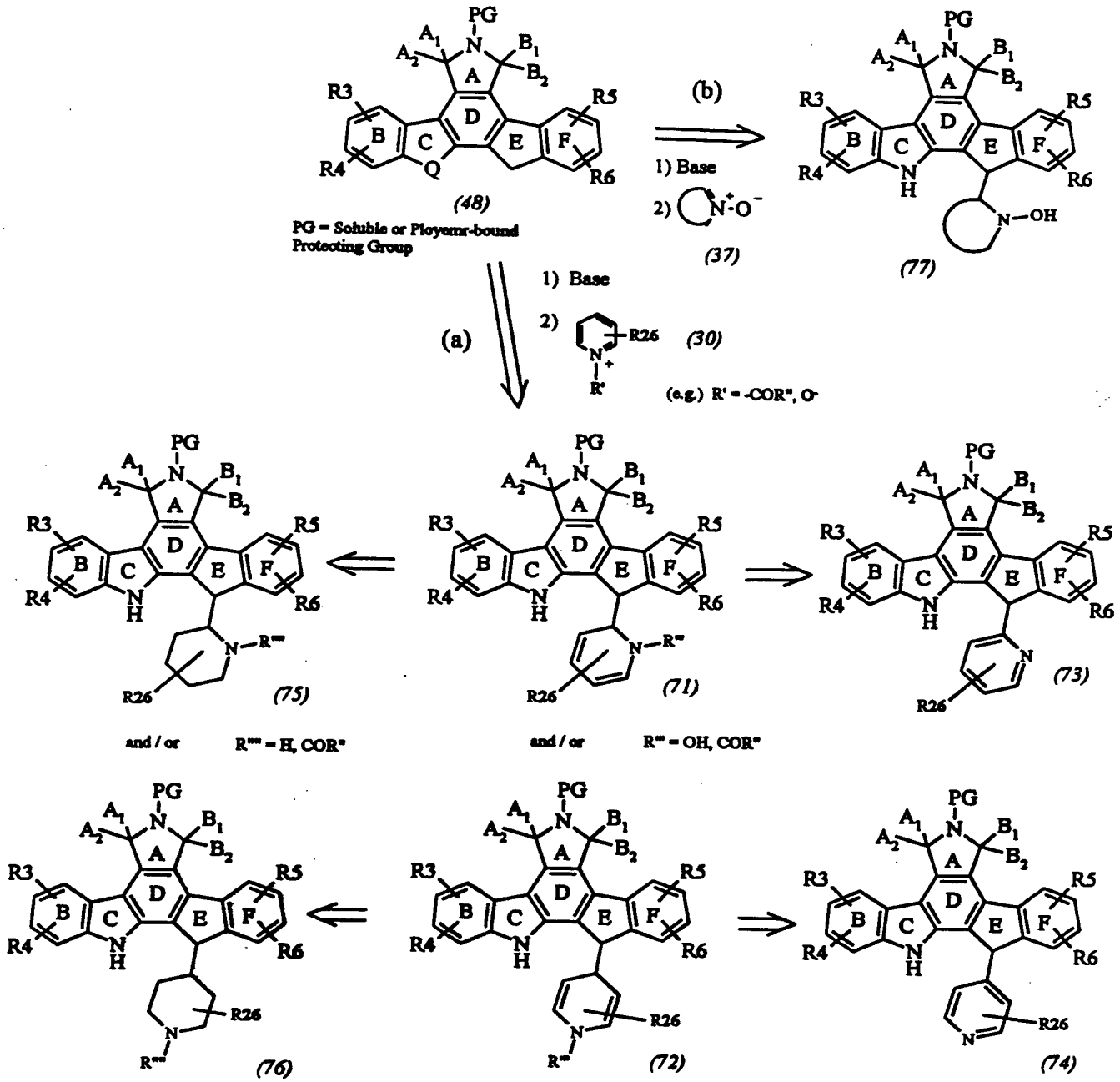
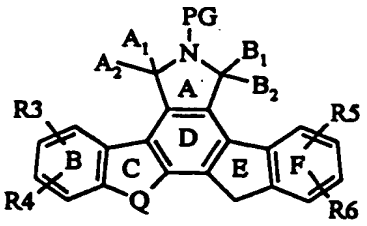

PG
A1
A2
B1
B2
A
R3
R5
D
B
C
E
F
R4
Q
R6
(48)
PG = Soluble or Ployemr-bound Protecting Group
(b)
1) Base
2)
(37)
(77)
N-OH
1) Base
2)
R26
(30)
(a)
R'
(e.g.) R' = -COR", O-
N
H
R"
(75)
and / or
R"" = H, COR"
(71)
and / or
R" = OH, COR"
(73)
(76)
(72)
(74)

Figure 18.

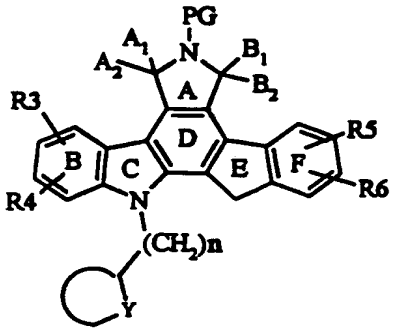


PG = Soluble or Ployemr-bound Protecting Group

(48)

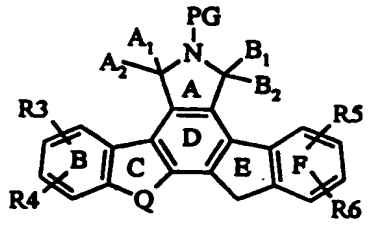
for Q =NH

1) Base
2) Y (CH2)n-X *(39)*

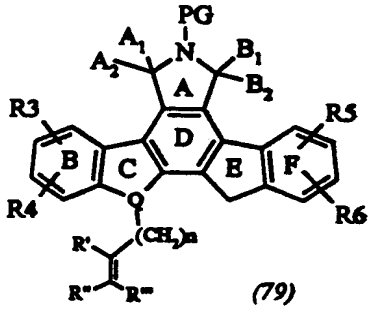


(78)

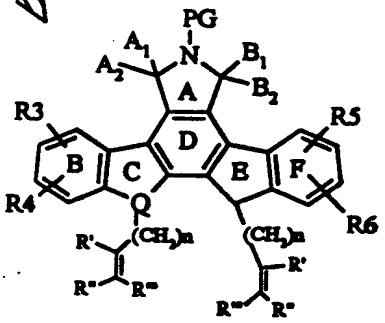
Figure 19.



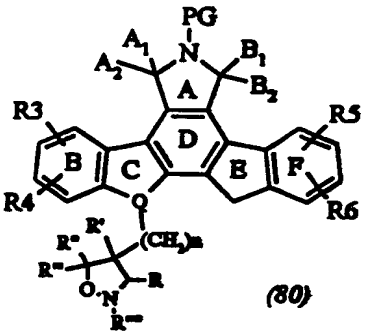
(48)



(79)

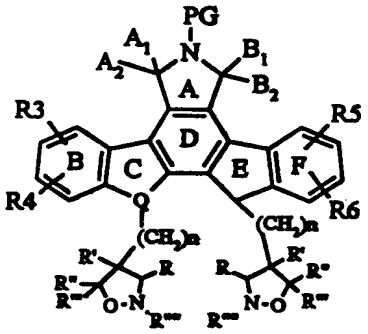


(82)



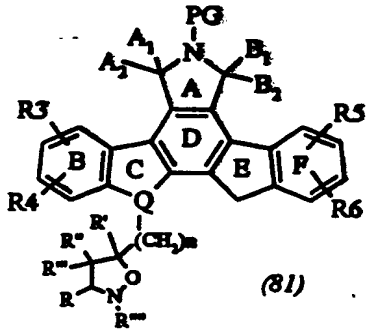
(80)

and/or

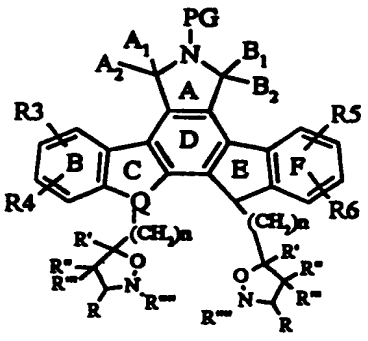


(83)

and/or



(81)



(84)

Figure 20.

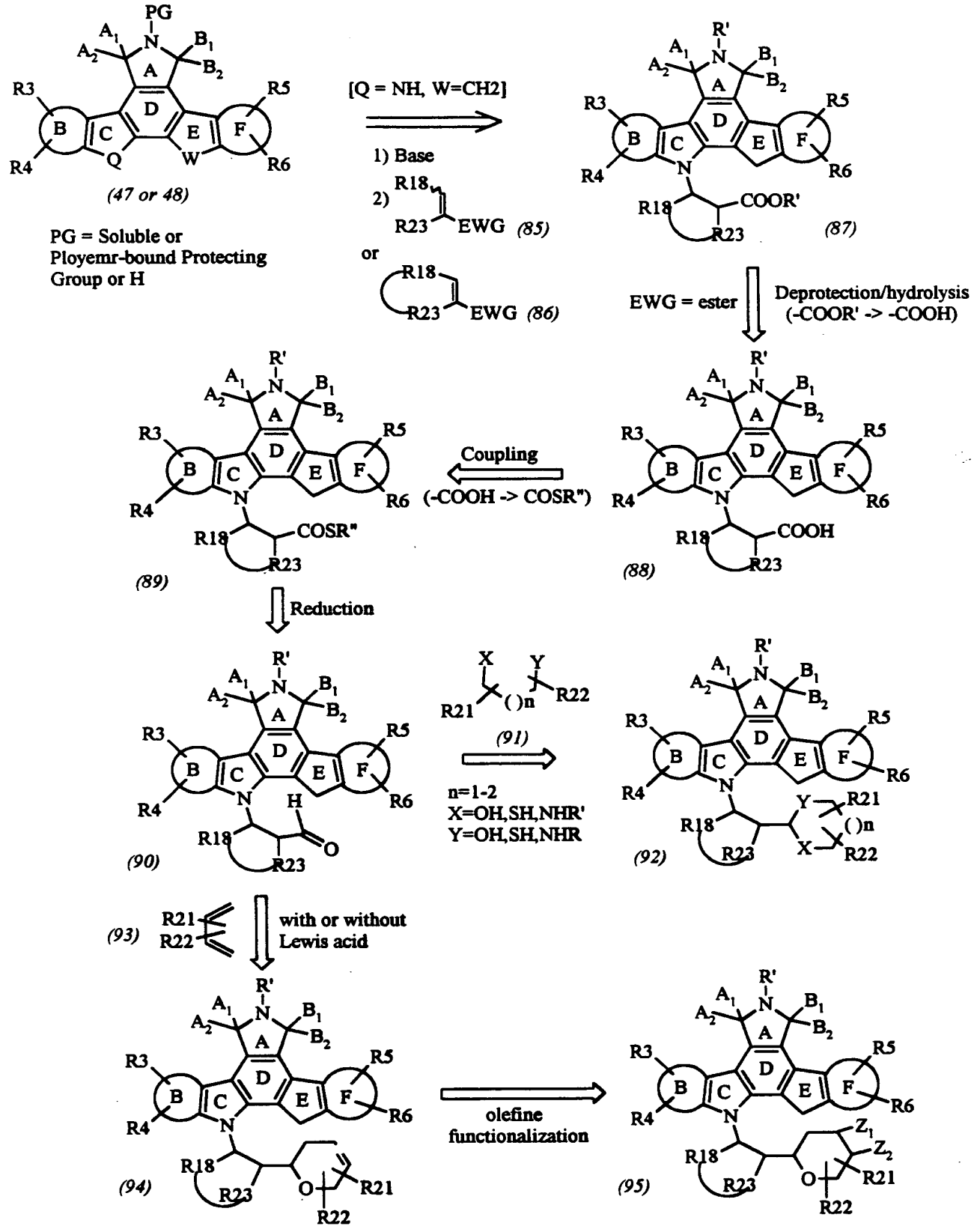
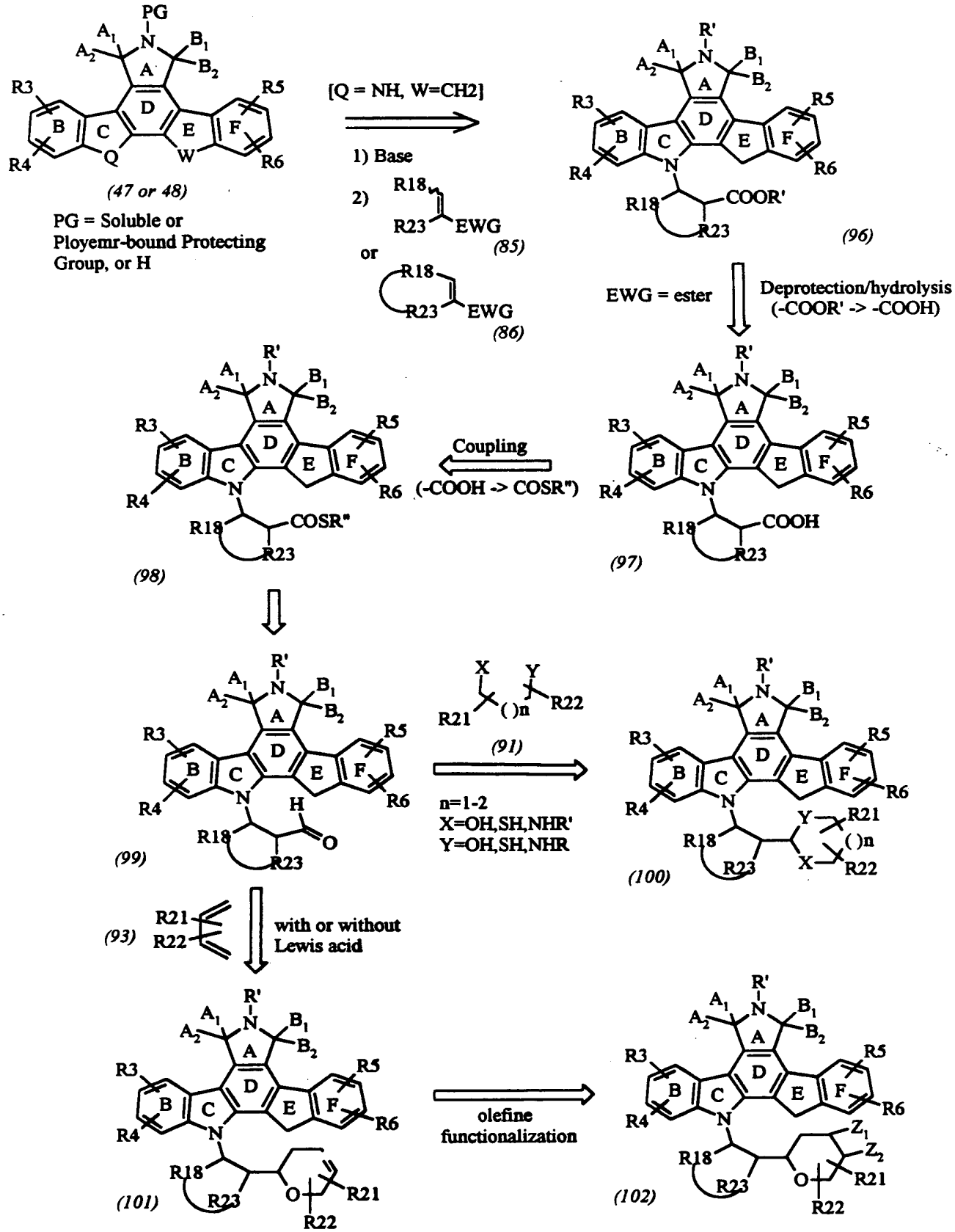

PG
A1
A2
N
B1
B2
A
R3
R5
D
B
C
E
F
R4
Q
W
R6
(47 or 48)
PG = Soluble or Ployemr-bound Protecting Group or H
[Q = NH, W=CH2]
1) Base
2)
R18
R23
EWG (85)
or
R18
R23
EWG (86)
R'
COOR'
(87)
EWG = ester
Deprotection/hydrolysis
(-COOR' -> -COOH)
COOH
(88)
Coupling
(-COOH -> COSR")
COSR"
(89)
Reduction
H
O
(90)
X
Y
R21
( )n
R22
(91)
n=1-2
X=OH,SH,NHR'
Y=OH,SH,NHR
(92)
(93)
with or without
Lewis acid
(94)
olefine
functionalization
Z1
Z2
(95)

Figure 21.


PG
A1
A2
N
B1
B2
A
R3
R5
D
B
C
E
F
R4
Q
W
R6
(47 or 48)
PG = Soluble or
Ployemr-bound Protecting
Group, or H
[Q = NH, W=CH2]
1) Base
2)
R18
R23
EWG
(85)
or
R18
R23
EWG
(86)
R'
COOR'
R18
R23
(96)
EWG = ester
Deprotection/hydrolysis
(-COOR' -> -COOH)
COOH
(97)
Coupling
(-COOH -> COSR")
COSR"
(98)
H
O
(99)
X
Y
R21
( )n
R22
(91)
n=1-2
X=OH,SH,NHR'
Y=OH,SH,NHR
(100)
(93)
with or without
Lewis acid
(101)
olefine
functionalization
Z1
Z2
(102)